

Effect of Ion Substitution on the Electrochemical Characteristics of Tunnel-containing Manganese Oxide Electrodes

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Li_xMnO_2 with the tunnel-containing $\text{Na}_{0.44}\text{MnO}_2$ structure has recently been used as a cathode material in both lithium/liquid electrolyte and lithium/polymer cells at 85 °C.^{1,2} Little or no capacity fading is seen during prolonged cycling in either configuration. The remarkable reversibility is particularly noteworthy in the elevated temperature cells, because the spinel LiMn_2O_4 tends to lose capacity rapidly when cycled in acidic electrolytes above 55 °C.³ Other desirable features of this material include phase stability to about 400 °C,⁴ resistance to degradation during over-charge or -discharge,⁵ and ability to discharge rapidly (up to 5C rate) without ill effect.¹ The characteristics of robustness and excellent reversibility are particularly attractive when the requirements for hybrid electric vehicle (HEV) batteries are taken into consideration: cost constraints mandate the use of inexpensive electrodes such as manganese oxides, but materials must demonstrate abuse-tolerance and be able to withstand thousands of high-power, shallow cycles.

For applications such as electric vehicles (EVs) or consumer devices, a higher specific energy may be required than what is currently provided by this material. Although the theoretical capacity, based on structural considerations, is about 200 mAh/g, only about half is utilized during a typical discharge. This is due to the sloping voltage profile; complete extraction of lithium ions occurs at potentials above the stability limits of common electrolytes. By chemically modifying the structure (e.g., by substitution of some of the Mn with other metals), it should be possible to alter the electrochemical characteristics and improve utilization without sacrificing cycle life or abuse-tolerance. Little is known, however, about the effect of substitution on the chemistry or electrochemistry of materials with the $\text{Na}_{0.44}\text{MnO}_2$ structure. We have undertaken a preliminary study to better understand these effects; the ultimate goal is to design a robust, high energy density electrode with the excellent cycling behavior of the parent compound.

Solid solutions with the $\text{Na}_{0.44}\text{MnO}_2$ structure are formed in the Na-M-Mn-O system when M is Ti or Cu,

for up to 55-atom % substitution (for Ti) and 11-atom % (for Cu). Lithiated analogs of the quaternary tunnel compounds can be made readily by ion exchange. When M is Ni, Fe, Co, and Zn, however, layered compounds form instead of the desired tunnel compound. When M is V, Zr, Nb, or Mo (or 22-atom % Cu), a phase mixture results.

Substituted tunnel compounds have markedly different discharge characteristics in lithium cells than the unsubstituted material. Figure 1 shows discharge profiles for Li/polymer cells containing Li_xMnO_2 and $\text{Li}_x\text{Ti}_{0.22}\text{MnO}_2$ at 85 °C. For the latter, the profile is more gradually sloping, with a slightly higher average voltage, allowing more capacity to be obtained between the voltage limits. The opposite is true for $\text{Li}_x\text{Cu}_{0.11}\text{Mn}_{0.89}\text{O}_2$ (Figure 2) discharged in Li/liquid electrolyte cells, and capacity between set voltage limits is markedly decreased compared to that of Li_xMnO_2 .

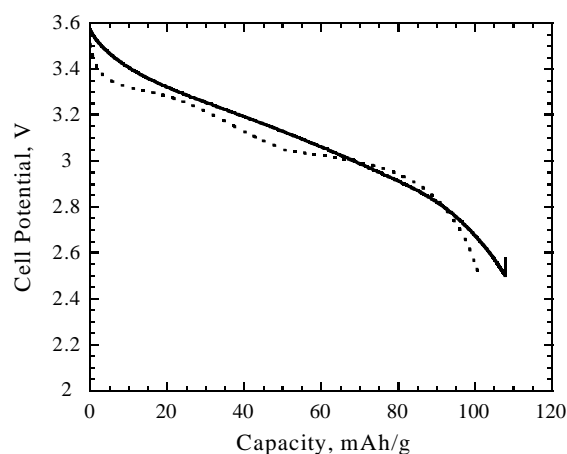


Figure 1. Discharges at 0.1 mA/cm² of Li/P(EO)₈LiTFSI cells at 85 °C with Li_xMnO_2 (---) or $\text{Li}_x\text{Ti}_{0.22}\text{Mn}_{0.78}\text{O}_2$ cathodes.

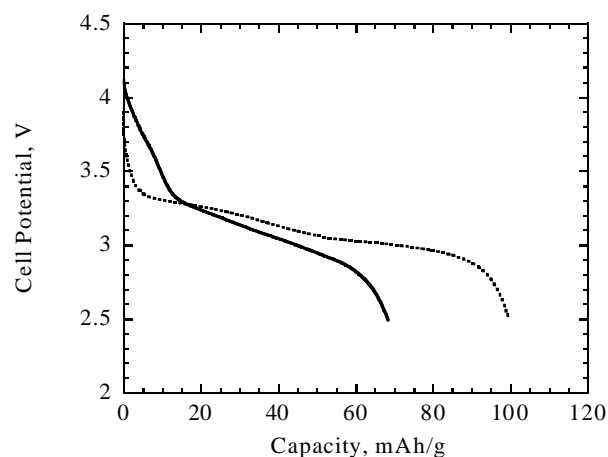


Figure 2. Discharges at 0.1 mA/cm² for Li/1M LiPF₆ cells with Li_xMnO_2 (---) or $\text{Li}_x\text{Cu}_{0.11}\text{Mn}_{0.89}\text{O}_2$ electrodes.

The changes in electrochemical characteristics can be understood in terms of relative unit cell size, the relative degree of replacement of electro-active Mn with electrochemically inert Ti or Cu, and the specific sites at which substitution takes place. These will be covered in detail at the presentation.

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